Quality Assessment Report for Water Quality Monitoring

October - December 2004

Submitted to the
Technical Oversight Committee

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I. Introduction

This report is an assessment of the SFWMD laboratory analysis and field sampling for Total Phosphorus (TP) monitoring primarily for the following projects/stations during the 4th quarter of 2004:

Conservation Area Inflow and Outflows (CAMB): S12A, S12B, S12C S12D, S333
Everglades National Park Inflow Monitoring (ENP): S175, S176, S177, S18C, S332, S332D
Everglades Protection Area (EVPA): LOX3 to LOX16
Non-Everglades Construction Project (NECP): S334

Since field QCs are collected for trips that include multiple project samples for the stations of interest, the report may also cover information on stations or project other than those listed above.

The District's Field Sampling Quality Manual states the minimum requirement followed in field sample collection. The Laboratory Quality Manual states the minimum requirement followed in laboratory sample preparation and analysis, as well as in data verification and validation. The results of laboratory and field quality control during this quarter are presented in Sections II and III of this report.

Included in this report is an analysis of the District's laboratory's performance on split and inter-laboratory studies with FDEP and other laboratories for three selected projects, i.e. EVPA, C111, for a one year period, National Proficiency Testing and USGS Analytical Evaluation Program for Reference Samples.

II. Field Sampling Quality Assessment

A. Quality Control

Field QC measures consist of equipment blanks (EB), field cleaned equipment blanks (FCEB), field blanks (FB), split samples (SS) and replicate samples (RS). Table 1 summarizes EB and FCEB results for all projects of interest to the TOC. Except for one blank result of the 119, all blanks were within the acceptance criteria. Table 2 summarizes field precision results. Field sampling precision was acceptable.

Data not meeting the set criteria for blanks, field precision or sampling protocols are flagged using FDEP data qualifier codes. A comprehensive list of flagged data for all trips that include samples for CAMB, ENP, EVPA and NECP during this quarter is presented in Table 3.

Table 1. Field and equipment blank results

Type of Blank	Project	# Blanks collected	% ≤0.002	% >0.002	Action Taken
EB	CAMB	8	100	0	
	ENP	1	100	0	
	EVPA	3	100	0	
	NECP	3	100	0	
FCEB	CAMB	62	100	0	
	ENP	13	92	1	blank was flagged
	EVPA	20	100	0	
	NECP	9	100	0	

Table 2. Field precision summary

Project Code	Numbers of triplicates	Mean % RSD	Comments
CAMB	5	11.3	Precision criteria were met (duplicate 25%, samples <PQL)
ENP	2	0.0	All triplicates <PQL
EVPA	3	13.7	Precision criteria were met.
NECP	1	6.3	Precision criteria were met.

Notes

1) All TP analyses were conducted by the District's Chemistry laboratory.
2) Field precision acceptance criteria: <20%. This criteria was applied only if sample values >PQL.
3) FB, FCEB and EB acceptance criteria: Must be ≤MDL.
4) Associated samples are flagged when concentrations are less than five times the resulting blank values for possibility of contamination.

Table 3. List of flagged data

Project	Date Collected	Station	Type	Flag Code	Comments
CAMB	14-Dec-2004	S5A	SAMP	PMF	Sample not flow proportional, missed 68 samples
CAMB	21-Dec-2004	USSO	SAMP	V	Sample associated with positive FCEB
ENP	21-Dec-2004	S18C	FCEB	V	FCEB>MDL
ENP	21-Dec-2004	S18C	SAMP	V	Sample associated with positive FCEB
NECP	5-Oct-2004	S9A	SAMP	!	PMF - possible particulate accumulation as a result of possible improper tubing placement, based on inspection performed on October 4, 2004.
CAMB	14-Dec-2004	S5A	SAMP	PMF	Sample not flow proportional, missed 68 samples
CAMB	21-Dec-2004	USSO	SAMP	V	Sample associated with positive FCEB
ENP	21-Dec-2004	S18C	FCEB	V	FCEB>MDL
ENP	21-Dec-2004	S18C	SAMP	V	Sample associated with positive FCEB
NECP	5-Oct-2004	S9A	SAMP	!	PMF - Historical outlier; possible particulate accumulation as a result of possible improper tubing placement, based on inspection performed on October 4, 2004.

Table 4. Samples not collected (Missing TPO4 results)

Project	Date Collected	Station	Type	Comments
CAMB	13-Dec-2004	S12A	SAMP	No flow, no sample collected
CAMB	13-Dec-2004	S12B	SAMP	No flow, no sample collected
CAMB	27-Dec-2004	S12C	SAMP	Gate closed, no flow, no sample collected
ENP	6-Cct-2004	S176	SAMP	No flow, no sample collected
ENP	3-Nov-2004	S176	SAMP	No flow, no sample collected
ENP	17-Nov-2004	S176	SAMP	Gate closed, no flow, no sample collected
ENP	15-Dec-2004	S176	SAMP	No flow, no sample collected
ENP	21-Dec-2004	S177	SAMP	Gate closed, no flow, no sample collected
ENP	27-Oct-2004	S18C	SAMP	Light flow through gates, no sample collected
ENP	24-Nov-2004	S18C	SAMP	Improper sample preservation
ENP	24-Nov-2004	S18C	SAMP	Improper sample preservation
ENP	29-Dec-2004	S18C	SAMP	Gate closed, no flow, no sample collected
ENP	21-Oct-2004	S332	SAMP	No flow, no sample collected
EVPA	18-Oct-2004	LOX3	SAMP	Sample not acidified
EVPA	13-Dec-2004	LOX5	SAMP	Tdepth<0.10 m, no sample collected
NECP	4-Oct-2004	S334	SAMP	Gate closed, no flow, no sample collected
NECP	27-Dec-2004	S334	SAMP	Gate closed, no flow, no sample collected

B. Field Audits

During this quarter, the following audits of field sample collection activities were performed for the following sampling groups:

1) United States Fish and Wildlife Service (USFWS) sampling team for the EVPA project - 12/13/2004
   The key findings were: a) lack of quality manual, b) unavailability of reference documentation in the field, c) inadequate field documentation, d) use of outdated preservation acids, and e) failure to quantitatively verify the range of field temperature and specific conductivity measurements. These deficiencies have been corrected except for the submission of the field quality manual which is still in draft.

2) SFWMD Sampling team for EVPA and NECP projects - 12/16/2004
   There were five key findings regarding inadequacy of or missing entries in field documentation. All deficiencies have been corrected.

3) Everglades National Park (ENP) sampling team for the EVER project - 12/13/2004
   The key findings were: a) collection was being done at 0.1 meter instead of mid-depth for sites with water depth between 0.1 and 1 meter, b)lack of a field quality manual, c) lack of personnel training records, d) unavailability of sampling reference documents in the field, e) inadequate documentation of field maintenance and calibration activities, f) lack of documentation of cleaning procedures, g) missing information on the chain of custody, h) no monitoring of intermediate storage refrigerator temperature, and i) inadequate and non-traceable records of acid preservation. Except for two items that still need correction, responses received were satisfactory to correct the deficiencies.

III. Laboratory Quality Control Assessment

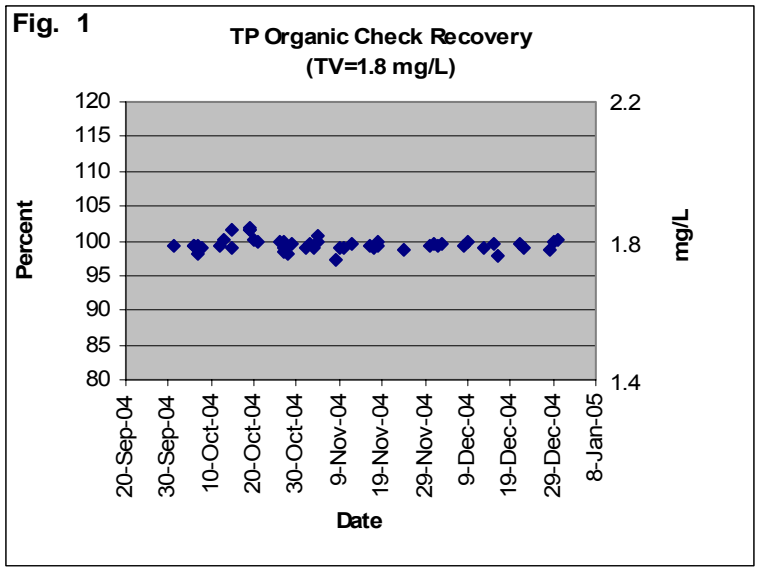
Routine laboratory QC samples include QC checks, matrix spikes, and precision checks. The charts presented in Figures 1-6 show recoveries from various levels of QC samples for the TP analysis at SFWMD laboratory. Statistical evaluation of precision and matrix spikes recoveries is also included. A portion of or an entire analytical run is generally rejected if QC recoveries are outside the set limits. Data is flagged accordingly if any deficiency is noted and the samples have exceeded the required holding times and can not be reanalyzed.

Recoveries for the QC samples are generally within $\pm$ 10% from the true value, which are acceptable. The MDL check (QC5), with a true value of 0.004 mg/L, had a mean recovery of 103.6%. The MDL check daily results indicate the laboratory consistently achieved the 0.002 mg/L MDL.

An organic check is a solution prepared from phytic acid, a stable form of organic phosphate. Recoveries for this check sample are between 97.4 – 101.8%, indicating that the digestion process was effective. The same material is used to prepare matrix spikes, the mean recovery for which was 100.8%

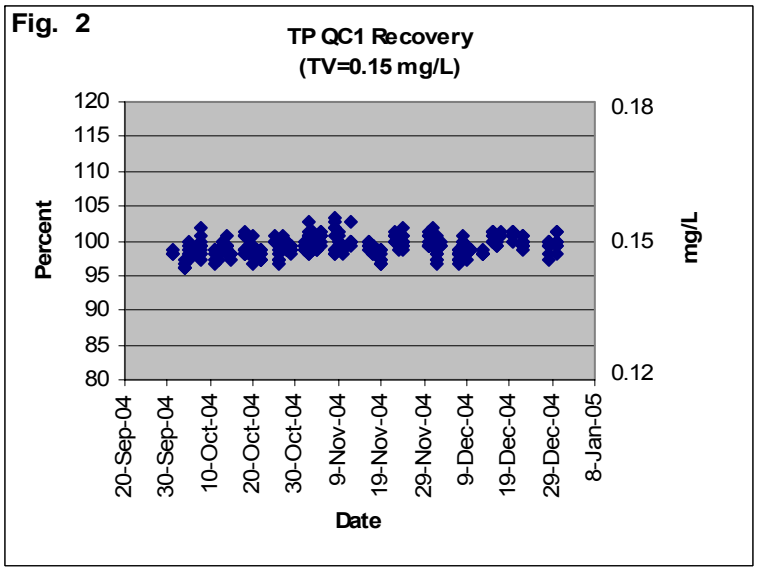
The precision target for TP analysis during this period was 10.0%, and as the report shows, mean %RPD was 1.7% and 1.2% for low (0 to 0.200 mg/L) and high level (0.200-2.00 mg/L) analyses, respectively. The maximum RPD during this period were 7.6% and 4.3% for low and high levels, respectively.

Fig. 1



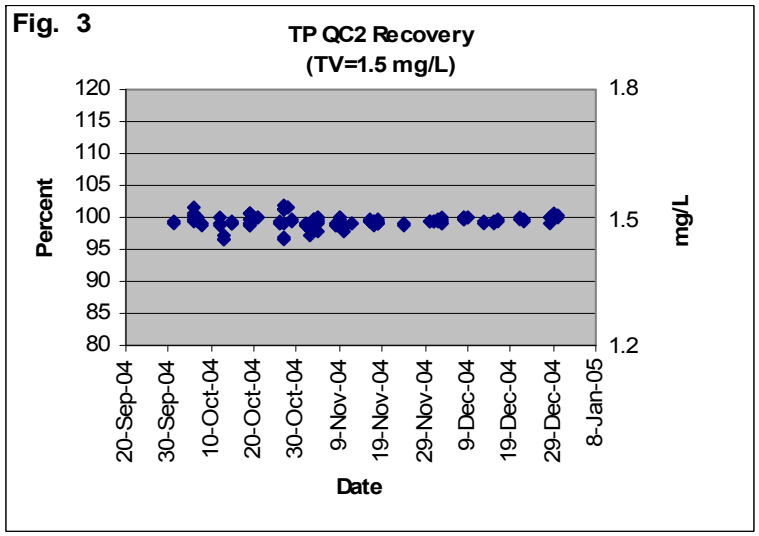
Mean = 99.5%, Max = 101.8%, Min = 97.4%

Fig. 2



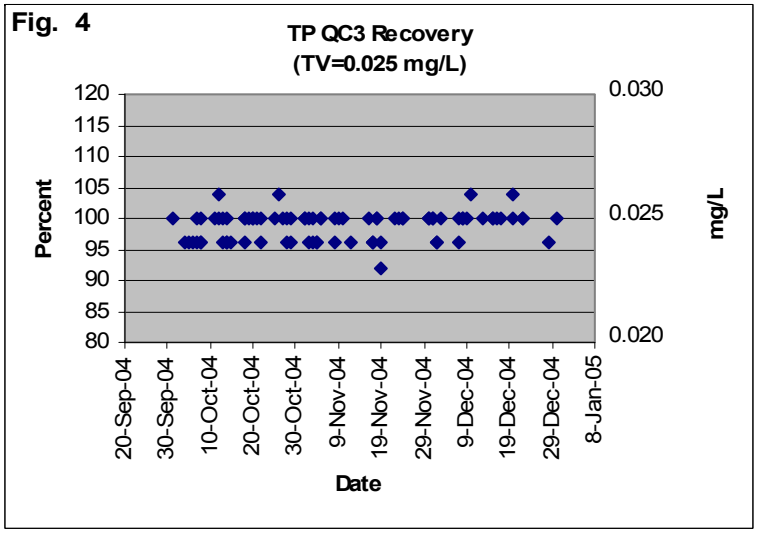
Mean = 99.2%, Max = 103.3%, Min = 96.0%

Fig. 3



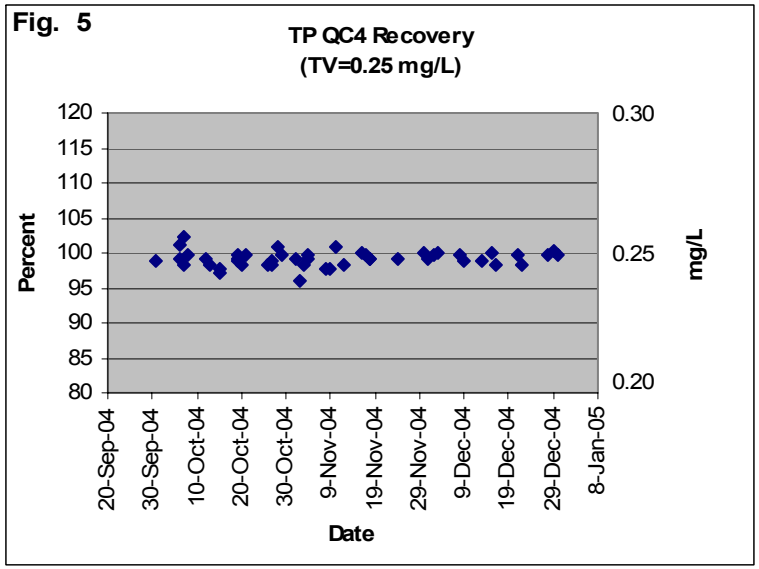
Mean = 99.4%, Max = 101.8%, Min = 96.6%

Fig. 4



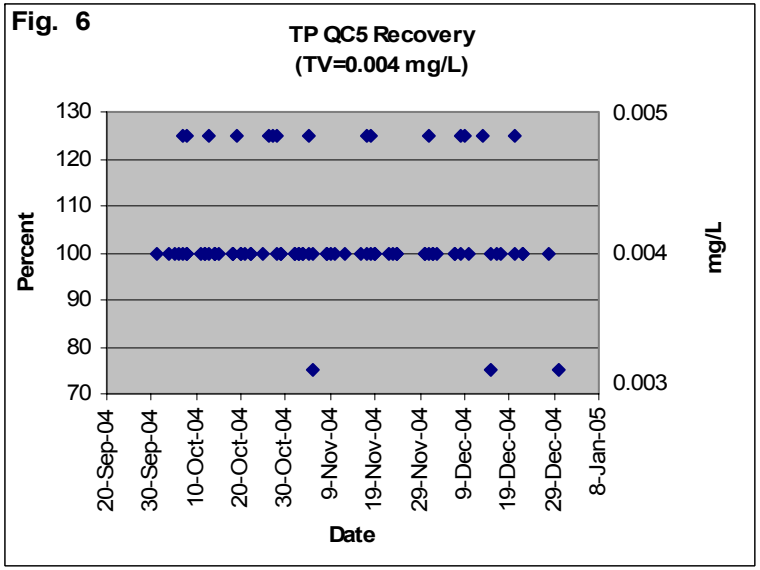
Mean = 98.8%, Max = 104%, Min = 92.0%

Fig. 5



Mean =99.2%, Max = 102.4%, Min = 96.0%

Fig. 6



Mean = 103.6%, Max = 125%, Min = 75.0%

TP Precision Data 10/1/04-12/30/04 Acceptance Limit = <10%			
Low Level (0-0.2)		High Level (0.2-2)	
Max	7.6	Max	4.3
Mean	1.7	Mean	1.2
Std Dev	1.57	Std Dev	1.03
3xSD	4.72	3xSD	3.08
UCL	6.4	UCL	4.2
n	253	n	57

TP Spike Recovery Data 10/1/04-12/30/04 Acceptance Limit = 90-110%	
Min	90
Max	110
Mean	100.8
Std Dev	3.33
3xSD	9.99
LCL	90.8
UCL	110.7
n	319

IV. Inter-Laboratory Quality Control Assessment

A. Split Studies

To continually assess comparability of results, the District sends split samples to other laboratories on a routine basis. Data from split studies between DEP and SFWMD laboratories from December 2003 to September 2004 for the following programs were used in this analysis: EVPA Quarterly Splits (EVPA), Everglades TP Round Robin (ERR), and S332 sites (C111).

The summary statistics and signed rank test for SFWMD vs. DEP TP results, as presented below, shows that the p-value for both <0.02 and >0.02 mg/L levels is 0.0176. However, the mean and median of differences from the two laboratories are <0.004. These are around the laboratories' MDLs; SFWMD's MDL is 0.002 mg/L while DEP laboratory's MDL is 0.004 mg/L. At these levels, wider variability can be expected even within each laboratory.

<0.02 mg/L

Summary Statistics

Lab	N	Mean	Median
FDEP	12	0.0128	0.0150
SFWMD	12	0.0096	0.0105

Statistical Test of Hypotheses

Summary Of Paired Differences		Hypothesis	Statistical Test	Pvalue
Mean Of Differences	-0.00317	Mean of Differences = 0		
Median Of Differences	-0.0035	Median of Differences = 0	**Signed Rank**	**0.0176**

>=0.02 mg/L

Summary Statistics

Lab	N	Mean	Median
FDEP	12	0.1098	0.106
SFWMD	12	0.1028	0.103

Statistical Test of Hypotheses

Summary Of Paired Differences		Hypothesis	Statistical Test	Pvalue
Mean Of Differences	-0.00708	Mean of Differences = 0		
Median Of Differences	-0.003	Median of Differences = 0	**Signed Rank**	**0.0176**

Regression analysis of the data set was done separately for TP>0.020 mg/L and for TP<0.020 mg/L. Logarithmic transformation was used for both ranges of TP concentration due to skewed distribution of data. Both regression analyses indicate that the slope is not significantly different from 1 and intercept is not significantly different from 0, indicating that both data sets are highly comparable (Figures 7 and 8).

These statistical analyses and findings were consistent with what was in FDEP Data Comparability Report (Nearhoff, presentation to TOC, 8/26/04).

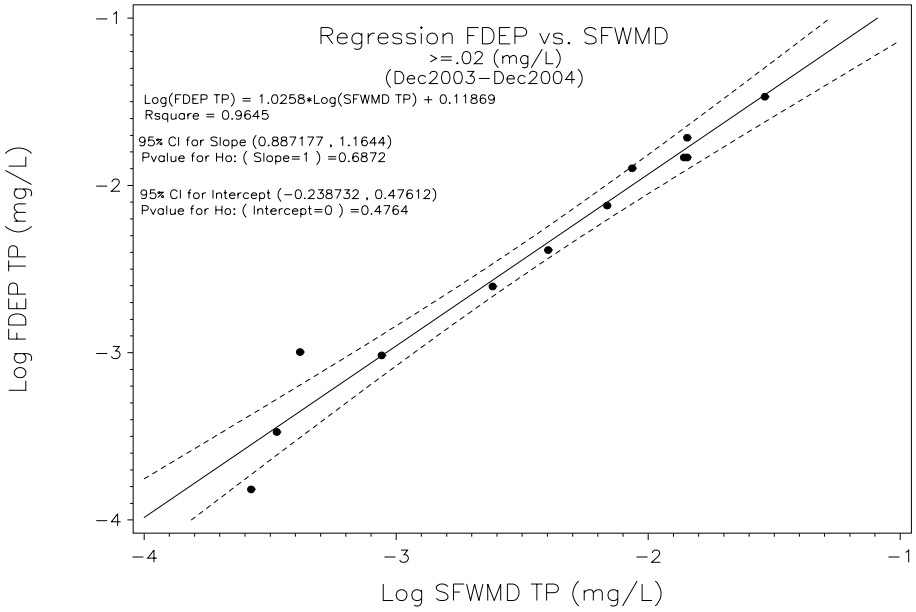


Fig.7. Regression Analysis for TP>0.020 mg/L

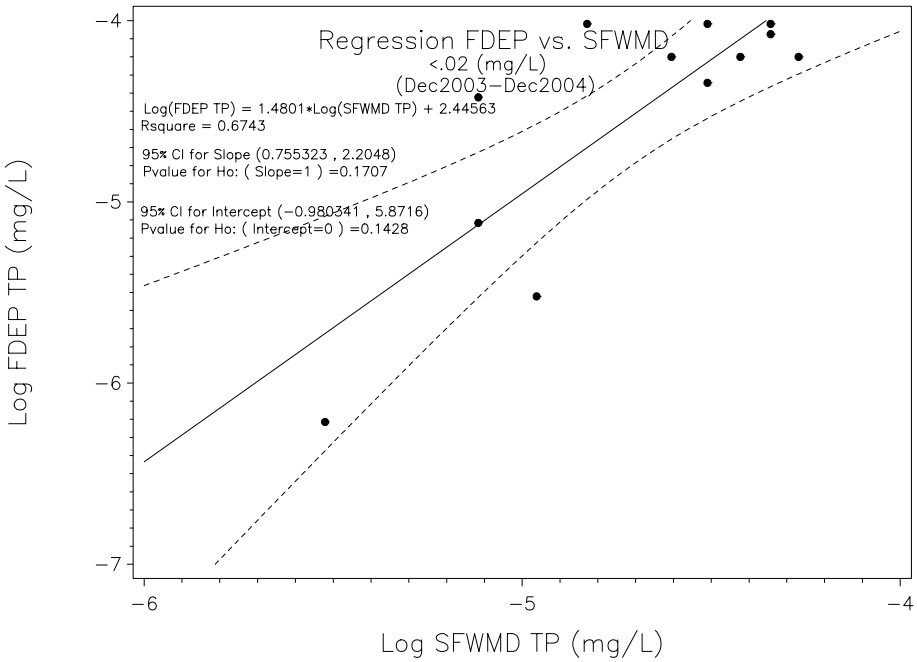


Fig. 8. Regression Analysis for TP <0.020 mg/L

Table 5. Results of TP split studies between SFWMD and FDEP laboratories, EVPA Project, December 2003 to December 2004.

Sample	Date	SFWMD	FDEP	% RPD/Comments
S332B-120903-1300	9-Dec-2003	0.006	0.012	<PQL
S332C-120903-1100	9-Dec-2003	0.007	0.004	<PQL
S332DDZE-120903-0800	9-Dec-2003	0.004	<0.004	<PQL
S339-120903-0000	9-Dec-2003	0.115	0.120	4.2
S339-120903-0800	9-Dec-2003	0.073	0.074	1.4
S339-120903-1600	9-Dec-2003	0.091	0.092	1.1
EVPA	15-Dec-2003	0.127	0.150	17
EVPA	15-Dec-2003	0.010	0.015	40.0; Heavy suspended solids
EVPA	15-Dec-2003	0.011	0.013	17.0; Heavy suspended solids
EVPA	15-Dec-2003	0.013	0.018	32.0; Heavy suspended solids
EVPA	8-Mar-2004	0.031	0.031	0
EVPA	8-Mar-2004	0.028	0.022	24.0; Heavy suspended solids
EVPA	8-Mar-2004	0.017	0.020	16
EVPA	8-Mar-2004	0.006	0.006	<PQL
EVPA	14-Jun-2004	0.047	0.049	4.2
EVPA	14-Jun-2004	0.034	0.050	38; Heavy suspended solids
EVPA	14-Jun-2004	0.158	0.160	1.2
EVPA	14-Jun-2004	0.156	0.160	2.5
EVPA	21-Sep-2004	0.215	0.230	6.7 Dark brown stain
EVPA	21-Sep-2004	0.008	0.018	76.9 Light brown stain
EVPA	21-Sep-2004	0.014	0.015	6.9 Light brown stain
EVPA	21-Sep-2004	0.012	0.015	22.2 Light brown stain
EVPA	13-Dec-2004	0.013	0.017	Light yellow stain, light solids
EVPA	13-Dec-2004	0.014	0.022	Dark yellow stain, light fine suspended solids
EVPA	13-Dec-2004	0.011	0.018	1-2 L bottle cracked and leaked, used only 1-2 L bottle
EVPA	13-Dec-2004	0.158	0.180	Brown stain, light suspended particles

B. National Proficiency Testing Results

As a requirement for laboratory certification, the District's laboratory performs proficiency testing (PT) on environmental samples on a semi-annual basis. This study is administered by vendors that have been approved by the National Institute of Science and Technology as PT providers for National Environmental Laboratory Accreditation Conference.

Table 6. The results of October 2004 PT study

Sample I.D	Reported Value, mg/L	Certified Value, mg/L	%Recovery	Status	Z-Score
Sample 1 (WP)	4.18	4.17	100.2	Acceptable	0.594
Sample 2 (APG)	9.39	9.71	96.7	Acceptable	0.0185

WP=water pollution; APG=Analytical Product Group, Inc.

C. U.S. Geological Survey Analytical Evaluation Program for Reference Samples

The District's laboratory participates in the USGS SRS Study on environmental samples semi-annually on a voluntary basis (Table 7). The Laboratory uses the study to monitor laboratory performance. Statistical analysis of results is conducted by the USGS, upon which laboratory results are based and performance is rated on a scale 0 to 4.

Rating	**Absolute Z-value (Rating based on)**
4 (Excellent)	0.00 to 0.50
3 (Good)	0.51 to 1.00
2 (Satisfactory)	1.01 to 1.50
1 (Marginal)	1.51 to 2.00
0 (Unsatisfactory)	>2.01

Table 7. USGS Study for TP, October 2004

Sample I.D	**Reported Value, mg/L**	**Most Probable Value, mg/L**	**%Recovery**	**Rating**	**Z-Value**
N-84	0.693	0.693	100	Excellent	0.00
N-83	0.154	0.155	99.4	Excellent	-0.10
M-172	1.34	1.35	99.3	Excellent	-0.19

Glossary

Equipment blank (EB). A general terminology used for analyte-free water that is processed on-site through all sampling equipment used in routine sample processing. May be an assessment of effectiveness of laboratory decontamination (LCEB) or on-site (field) decontamination (FCEB). EB values are indicative of the effectiveness of the decontamination process.

Field Cleaned Equipment Blank (FCEB). Analyte-free water that is processed on-site, after the first sampling site, through all sampling equipment used in routine sample processing. EB values are indicative of the effectiveness of the decontamination process.

Field blank (FB). Analyte-free water that is poured directly into the sample container on site during routine collection, preserved and kept open until sample collection is completed for the routine sample at that site. FB values are indicative of environmental contamination on site.

Split sample (SS). A second sample collected from the same sample obtained from the same sampling device. Results for SS are compared with routine sample results; agreement between these two results is mostly an indication of laboratory precision.

Replicate sample (RS). A second sample collected from the same source as the routine sample, using the same sampling equipment. RS data are compared to routine sample to evaluate sampling precision.

Precision. The agreement or closeness between two or more results and is an indication that the measurement system is operating consistently and is a quantifiable indication of variations introduced by the analytical systems over a given time and field sampling period.

Accuracy. The agreement between the actual obtained result and the expected result. QC check samples having known or "true" value are used to test for the accuracy of a measurement system.

Method Detection Limit (MDL). The smallest concentration of an analyte of interest that can be measured and reported with 99 percent confidence that the concentration is greater than zero. The MDL's are determined from the analysis of a sample in a given matrix, using accepted sampling and analytical preparation procedures, containing the analyte at a specified level. The MDL is determined by the protocol defined in section 40 CFR Part 136, Appendix B as established by the EPA.

Practical Quantitation Limit (PQL). The smallest concentration of an analyte of interest that can be quantitatively reported with a specific degree of confidence. Generally, the PQL is 12 times the standard deviation that is derived from the procedure used to determine the MDL, or can be assumed to be 4 times the MDL.

Relative Standard Deviation (RSD). A measurement of precision, used when comparing more than two results. It is calculated as: %RSD = [Std. Deviation/Mean]*100

Relative Percent Difference (RPD). A measure of precision, used when comparing two values. It is calculated as: %RPD = [Value1-Value2]/Mean * 100.